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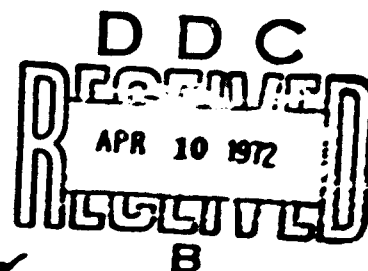
EFFECTS OF SEA WATER ON CONCRETE

by

Bryant Mather



December 1964



U. S. Army Engineer Waterways Experiment Station
CORPS OF ENGINEERS
Vicksburg, Mississippi

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FOREWORD

This paper was prepared at the request of Mrs. Katharine Mather, Chairman, Subcommittee MC-B2(5) of Committee MC-B2 on Performance of Concrete--Chemical Aspects of the Concrete Division, Department of Materials and Construction, Highway Research Board (HRB), National Academy of Sciences-National Research Council. Subcommittee MC-B2(5) was charged by Committee MC-B2 with the organizing of a Symposium on Effects of Aggressive Fluids on Concrete to be held at the 44th Annual Meeting of HRB, Washington, D. C., January 1965. The paper has been reviewed and approved for presentation and publication by the Chief of Engineers, U. S. Army, and by Committee MC-B2 of HRB.

Preparation of the paper was accomplished at the Concrete Division, U. S. Army Engineer Waterways Experiment Station, under the direction of Mr. Thomas B. Kennedy.

Director of the Waterways Experiment Station during preparation of the paper was Col. Alex G. Sutton, Jr., CE. Technical Director was Mr. J. B. Tiffany.

EFFECTS OF SEA WATER ON CONCRETE*

by

Bryant Mather**

Synopsis

Concrete exposed to sea water is wetted by a solution of salts-- principally sodium chloride and magnesium sulfate. Damage to concrete, if it occurs, usually results from failure to use good practices in concrete construction, and often is the result of freezing and thawing or wetting and drying as much as or more than the results of the effects of sea water as such. Magnesium sulfate may attack most, if not all, of the constituents of hardened portland cement paste, especially the aluminate constituent; chlorides may promote corrosion of steel; and alkalies may participate

* Prepared for inclusion in Symposium on Effects of Aggressive Fluids on Concrete sponsored by Committee MC-B2 on Performance of Concrete-- Chemical Aspects, at 44th Annual Meeting, Highway Research Board, January 1965; presentation and publication approved by the Chief of Engineers, U. S. Army, Washington, D. C., 28 October 1964.

** Supervisory Research Civil Engineer, Chief, Engineering Sciences Branch, Concrete Division, U. S. Army Engineer Waterways Experiment Station, CE, Jackson, Mississippi.

in alkali-aggregate reaction.¹ Thus, concrete exposed to sea water should be made with cement of controlled aluminate content and with nonreactive aggregate; embedded steel should be well covered by concrete of low permeability; and good construction practices should be followed.

Introduction

Concrete has been employed in construction exposed to the action of sea water for as long as concrete has been used. Examples of concrete used by the Romans 2000 years ago in structures exposed to sea water on the shores of the Mediterranean Sea are still intact. When concrete is to be employed under conditions in which it will be exposed to the effects of sea water, cognizance should be taken of these effects and appropriate precautions taken. However, generally, these precautions are not drastic, and do not involve the selection and use of unusual materials or procedures nor cause any significant increase in cost of production.^{12*}

The effects of sea water on concrete may conveniently be examined by considering, first, the factors characteristic of the sea-water exposure that can affect concrete; second, the elements of the specific concrete involved that may be affected by these factors; third, the consequences of the interaction of sea water with the concrete; and, finally, the precautions that should be taken to avoid undesirable performance of the concrete due to its interaction with sea water.

* Raised numerals refer to similarly numbered items in list of references at end of this paper.

Pertinent Factors in a Sea-Water Exposure

Concrete exposed to sea water will be subjected to wetting by an aqueous solution containing principally dissolved sodium chloride and magnesium sulfate. The oceans contain on the average about 35 parts per thousand (3.5 percent) of dissolved salts. The major cations, Ca^{++} , Mg^{++} , Na^+ , and K^+ , exist in sea water largely as uncomplexed species. The major anions include Cl^- , which is also not strongly complexed, and $\text{CO}_3^{=}$, HCO_3^- , and $\text{SO}_4^{=}$, which are. Expressed as milligrams per liter of sea water, the principal elements present in solution are: chlorine, 19,000; sodium, 10,600; magnesium, 1300; sulfur, 900; calcium, 400; and potassium, 380. All other elements are probably present, but no others make up more than 65 milligrams per liter. The six elements mentioned make up 99 percent of the dissolved salts in sea water. Although the concentration of dissolved solids has been found to vary from place to place, the ratio of any one of the major constituents to the total dissolved solids is nearly constant everywhere. The foregoing information, taken from a recent report,² can be compared with the following analysis of a specific sample reported by Forrest and Worthley.⁴

Analysis of Sea Water from St. Vincent Gulf, South Australia
Specific Gravity of Sea Water (25 C) = 1.03

<u>Ion</u>	<u>Concentration (g/100 ml)</u>	<u>Ion</u>	<u>Concentration (g/100 ml)</u>
Na^+	1.22	Cl^-	2.19
Mg^{2+}	0.145	SO_4^{2-}	0.32
Ca^{2+}	0.056	HCO_3^-	0.014
K^+	0.044	Br^-	0.008

Thus, the factors inherent in sea-water exposure that should be considered for their effects on concrete are: wetting and drying, chemical reaction of chlorides, sulfates, and alkalies (sodium and potassium), and in some instances, dissolved carbon dioxide.

The elements of concrete that may be affected by wetting or by chemical reaction with chlorides, sulfates, or alkalies include the cement, the aggregates, and reinforcing steel or other metal, if present.

Effects of Continuous Immersion of Concrete in Sea Water

Concrete that is totally and continuously immersed in water, even if the water contains dissolved salts such as are found in sea water, generally may be regarded as being in a protected exposure. Continuous immersion usually provides a uniformity of environment with respect to temperature and moisture content that prevents the immersed concrete from being subjected to such deteriorating influences as frost action, volume change due to wetting and drying, and differential volume change due to moisture content differences between the surface and the interior. Continuous immersion also tends to reduce the potential for chemical reaction by removing changes in degree of saturation as a mechanism for the flow into and out of the concrete of solutions containing ions that are capable of attacking constituents of the concrete, and leaving only concentration gradients as the means of ingress of such ions. Locher and Pisters¹¹ note that, under equal conditions of exposure, the aggressiveness of water increases with increasing concentration of the relevant substances, but that aggressiveness is also increased by higher temperatures, higher pressures, wetting and drying, or mechanical abrasion by fast-flowing or turbulent waters.

Effects of Intermittent Immersion of Concrete in Sea Water

Most concrete structures exposed to sea water are partially or wholly situated so that they are sometimes immersed in sea water and sometimes exposed to the air. If the structure is located where the temperatures fall below freezing, then the concrete that is exposed to the air with falling tide is probably subjected to as severe frost action as is any concrete in natural exposure. The realization that concrete exposed in the tidal zone in a region of low winter temperatures would be subjected to very severe frost action resulted in the selection of the mean-tide elevation at Treat Island, Cobscook Bay, Maine, as the location for the U. S. Army Corps of Engineers severe natural weathering station. This location has been used since 1936 by the Corps of Engineers to develop information rapidly on the relative resistance of concretes to frost action.⁸ Since effects of frost action on concrete are not within the scope of this symposium, this subject will not be developed further here.

The second important effect on concrete related to wetting and drying is the volume change relations due to changes in, or changes in uniformity of, moisture content. These phenomena, often referred to as "drying shrinkage" effects, are also not within the scope of this symposium, and hence will not be discussed further here.

In localities such as Treat Island, Maine, the mean temperature of the sea water is low and chemical reactions take place relatively slowly. Concretes that are relatively deficient in resistance to frost action seldom survive long enough to manifest any readily observable effects of chemical attack; hence, it can be argued that there is a general

tendency for the severity of chemical attack to be reduced when that of physical attack increases, and vice versa.⁸

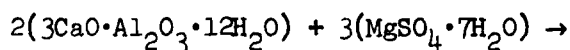
Chemical Attack of Sea Water on Concrete

The potentially aggressive constituents of sea water with respect to concrete are the sulfate, chloride, carbonate, bicarbonate, alkali metal, and magnesium ions. The aggressive action of the sulfate ion on concrete is being discussed by other contributors to this symposium.* However, since, in sea water, the sulfate component is magnesium sulfate rather than sodium or calcium sulfate, as is more often the case in sulfate-attack situations not involving sea water, the various chemical reactions of magnesium sulfate with several of the constituents of hydrated portland cement are noted subsequently. These comments are based on the discussion by F. M. Lea⁹ who pointed out that, initially, magnesium sulfate has a similar action to that of other sulfates in attacking calcium aluminate hydrate, but that later it can induce a significantly different and more far-reaching effect because of its ability--as distinguished from other sulfates--to attack and decompose the calcium silicate hydrate. This reaction (equation 4) proceeds to completion due to the low solubility of magnesium hydroxide.

Magnesium sulfate

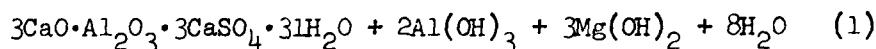
Magnesium sulfate initially reacts with calcium aluminate hydrate to form calcium aluminum sulfate hydrate (ettringite), magnesium hydroxide, and aluminum hydroxide:

* W. C. Hansen, "Attack on Portland Cement Concrete by Alkali Soils and Waters: A Critical Review."



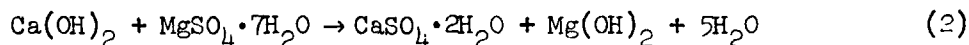
calcium aluminate
hydrate

magnesium
sulfate

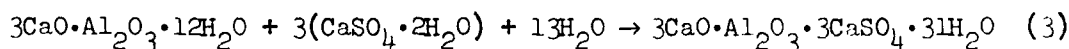


calcium aluminum sulfate aluminum magnesium
hydrate (ettringite) hydroxide hydroxide

Magnesium sulfate also reacts with calcium hydroxide to form calcium sulfate, which, in turn, reacts with calcium aluminate hydrate to form additional calcium aluminum sulfate hydrate (ettringite):

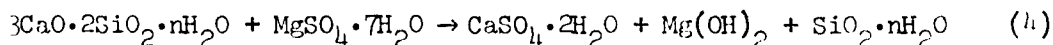


calcium magnesium calcium sul- magnesium
hydroxide sulfate fate (gypsum) hydroxide



calcium aluminate calcium sulfate calcium aluminum sulfate
hydrate (gypsum) hydrate (ettringite)

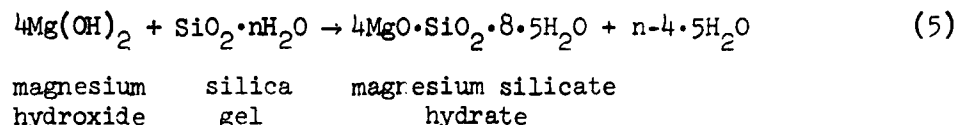
Magnesium sulfate also can react with calcium silicate hydrate to form calcium sulfate, magnesium hydroxide, and silica gel.



calcium silicate magnesium calcium sul- magnesium silica
hydrate sulfate fate (gypsum) hydroxide gel

The calcium sulfate formed in equation 4 may then react with calcium aluminate hydrate according to equation 3.

Finally, the magnesium hydroxide formed in the reactions indicated by either equations 1 or 4 can react with silica gel, as produced by the reaction indicated in equation 4 or otherwise, to form a magnesium silicate hydrate.



A soft white material having the approximate composition

$4\text{MgO} \cdot \text{SiO}_2 \cdot 8.5\text{H}_2\text{O}$ was found by Cole³ in a deteriorated concrete seawall.

Carbonate and bicarbonate

The carbonate and bicarbonate ions may participate in the reaction of carbonation of calcium ion or calcium hydroxide formed during hydration of cement. In a discussion¹⁶ of deterioration of concrete in the shipways at Newport News, Virginia, in 1948, Mrs. Terzaghi concluded that two processes were at work, one involving sulfate attack that caused internal expansion and cracking, and the other involving carbon dioxide dissolved in the water as carbonic acid that caused local softening and disintegration. The water samples taken from relief wells in these shipways were regarded as containing from 30 to 60 percent sea water, based on chloride content, and had free CO_2 contents of 7 to 99 mg per liter, the highest CO_2 content being in the sample of lowest sea-water content which had 57 mg per liter of aggressive CO_2 and a pH of 6.9.

Alkalies

The alkali metal ions may participate in any of several reactions with reactive silica or reactive carbonate constituents of the aggregates. Stanton¹⁵ in 1937 listed among structures adversely affected by alkali-silica reaction sections of seawalls in Ventura and Santa Barbara Counties in California. Recently it was suggested that expansion of concrete in certain dry docks in New York had resulted from the alkali-carbonate reaction. The available data, however, indicated that the aggregates in these

structures are natural siliceous sand and gravel. Hence, so far as is known, there have as yet been no documented cases of alkali-carbonate reaction which have caused deterioration of concrete structures exposed to sea water. Kennedy and Mather⁸ found that in concrete containing a crushed limestone aggregate that had been exposed to sea water at Treat Island, Maine, there was evidence of the formation of reaction rims on certain limestone coarse-aggregate particles. The particular limestone studied by them contained about 4 percent of a montmorillonitic clay which undergoes greater swelling when wetted with a solution containing sodium ion than when sodium ion is not present. They showed that this material, processed as manufactured fine aggregate, exhibited two to three times as much increase in volume when immersed in sea water as when immersed in fresh water or in a saturated solution of calcium hydroxide.

Chlorides

The chloride ion may participate either in chemical reactions similar to those involving the sulfate ion--so as to yield such products as chloraluminates that are analogous to sulfoaluminates--or in the reactions involving the corrosion of reinforcing or other embedded metal. In this latter connection Halstead and Woodworth⁶ reported that reinforced concrete structures exposed under coastal conditions (within 10 miles of the sea coast) in South Africa have in some cases shown deterioration believed to have been caused by electrochemical corrosion of the steel. In the discussion of their paper it was noted that the South African Railway Administration has adopted the policy of using reinforced concrete structures in preference to steel because of difficulties in maintaining steel structures. This agency also has attempted to design structures for a minimum

of reinforcing steel. The performance of such structures has generally been good, and such deterioration as has occurred is believed related to insufficient concrete cover over reinforcing steel that permitted corrosion to occur.

The role of chlorides in sea water in chemical interaction with concrete is twofold. Chlorides act independently to do those things that chlorides are capable of doing, and they also tend to retard or inhibit the action of sulfates. The presence of chlorides, as in sea water, retards or inhibits the expansion of concrete by sulfate solutions, though not the degree of reaction. Lea⁹ cited the work of Batta, who attributed this effect to the greater solubility of gypsum and calcium aluminum sulfate in chloride solutions, and it is the reason why failure arising from chemical attack by sea water is not preceded by swelling to the same degree as in solutions of sodium or magnesium sulfate.

Griffin and Henry⁵ studied, separately, the effects of sodium chloride and sea-water salts in concrete. Their purpose was to determine the effect of sea-salt spray on concrete and the permissible amounts of salt in concrete when it is mixed. They found the optimum salinity of mixing water for maximum compressive strength to be from 18 to 36 g/kg when sodium chloride was used, and up to 36 g/kg when sea salt was used. They also found that, when sodium chloride was used, the rate of moisture migration through concrete from a region of higher to one of lower relative humidity increased with increasing salinity of mixing water to a salinity of about 70 g/kg, and then remained relatively constant with further increase in salinity. When sea salt was used, the rate of moisture migration also increased with increase in salinity, but leveled off at about 25 g/kg.

They concluded that some salt may be beneficial to concrete in some respects. With a mixing water salinity of about 25 g/kg the strength was improved, the rate of moisture movement was reduced, and corrosion of mild steel in the low-strength concrete used in their investigation was negligible. With sodium chloride, the maximum corrosion of mild steel appeared to take place at a salinity of about 70 g/kg. It should perhaps be emphasized that Griffin and Henry were studying the "permissible amounts of salt" that could be tolerated; it is not, I believe, their intent to suggest that one would deliberately add salt to reinforced concrete if it could readily be avoided.

Work done in connection with studies of the action of chloride salts used to remove ice from concrete pavements, insofar as it concerns the effect of chloride ion, may be considered relevant to the action of sea water. Hartmann⁷ has noted that the reaction of sodium chloride solutions with tricalcium aluminate or tricalcium aluminate hydrates is to produce either or both the calcium chloraluminate hydrates $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$ or $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 18\text{H}_2\text{O}$. However, she concluded that, while a chemical effect of chloride deicing salts on concrete was a possible cause of damage, it did not seem to be a probable cause.

Factors Affecting Resistance of Concrete to Chemical Attack

Results of experiments in which mortars and concrete specimens have been exposed to sea water are in general agreement that the attack occurs to the extent that hydrated calcium aluminate is available and accessible to the sulfates in the sea water. The more permeable the concrete and the higher the C_3A content of the cement, the sooner will evidence of sulfate

attack be manifested and the greater will be the degree of attack.

The use of pozzolans in concrete to be exposed to sea water has long been advocated because of observations that their use increases the resistance of the concrete to chemical attack of the sea water. Lea⁹ reviewed the various explanations that have been offered for this effect, and concluded that many or all of them sound reasonable. However, he also concluded that no one of them by itself provides an adequate explanation, and that all of them taken together fail to give the complete story. The explanations include: (1) reduction in amount of free calcium hydroxide by reaction with pozzolan, thus reducing the degree to which the reaction of sulfates and calcium hydroxide can occur; (2) increased solubility of hydrated calcium aluminates with decreased concentration of calcium hydroxide, and hence greater likelihood that the sulfate-aluminate reaction will take place through solution rather than in the solid state and thus produce less expansion; (3) decreased tendency of the low-sulfate calcium aluminum sulfate to convert to the high-sulfate form (ettringite) as the concentration of calcium hydroxide in solution decreases, due to the higher sulfate concentration required to effect the conversion as such decrease occurs; (4) decreased permeability of the concrete with reduced rate of entry of sulfate solution; (5) formation of lime-pozzolan reaction product films that protect the hydrated calcium aluminate; and (6) decomposition of lime-pozzolan reaction products by sea water to leave silica and alumina gels which are more stable products.

Satisfactory concrete for exposure to sea water will be obtained if reasonable precautions are followed in the selection and use of the materials of which it is composed. The 1963 ACI Standard Building Code¹

requires that concrete that is to be exposed to freezing while wet shall have a water-cement ratio not exceeding 6 gal per bag and shall contain entrained air. It references ACI 613-54¹ for requirements for sea-water exposure, table 4 of which requires that water-cement ratios not exceed 4-1/2 gal per bag for thin members and 5 gal per bag for thicker members in contact with sea water. The cement should meet the requirements for type II, specifically in that it should not contain more than 8.0 percent tri-calcium aluminate (C_3A) as calculated from the chemical analysis. Reinforced concrete members should be designed and inspected continuously during construction to ensure that no steel is closer than 3 in. from the exposed faces and 4 in. from corners, unless special precautions are taken to prevent corrosion.

Special treatments and special materials may, in certain cases, prove advantageous. Wakeman and his associates have described¹⁷ the successful use of asphalt impregnation of precast concrete piling to improve resistance to sea-water exposure. Li¹⁰ has called attention recently to the potential benefits of expansive cements for concrete construction in marine exposures. Portions of his statement are summarized as follows: Concretes made with expansive cement may be controlled to achieve shrinkage compensation, resistance to cracking, reduced permeability, and wear resistance. Such properties may help to render wharf decks crackproof, waterproof, and hence more wear-resistant. Expansive-cement concrete should further enhance the resistance to sea water of both reinforced and prestressed concrete piles for waterfront applications.

Neville¹⁴ notes that portland blast-furnace slag cement is frequently used in sea-water construction because of the fairly high sulfate

resistance of concrete made with it, and that concrete made with aluminous cement stands up extremely well in sea water. He points out that sea water, however, should not be used as mixing water when aluminous cements are used.

The performance of portland-cement concrete when used in service involving exposure to sea water has often been excellent, usually adequate, but sometimes exceedingly poor. It is believed that, when poor performance has occurred, the cause was poor concrete, the inferior nature of which was perhaps revealed more rapidly by the somewhat more severe exposure than might have been the case in a less severe situation. Mention was made earlier of concrete which has been exposed to Mediterranean Sea water for 2000 years and is in rather good shape.

Examples of Performance of Reinforced Concrete in Maritime Exposures

Wentworth-Shields²¹ described the first maritime reinforced concrete structure in Great Britain, constructed at Southampton in 1899, and noted that very few failures have occurred. The 1899 structure was a jetty consisting of a 100- by 40-ft deck on piles. In 1902, Town Quay was built at Southampton--a reinforced concrete structure 360 by 20 by 34 ft high. A few years later longitudinal cracks appeared above the mean tide level along lines of reinforcement, due to rusting of steel. Repairs were made with pneumatically applied mortar. The rusting of the steel has been ascribed to the permeability of the concrete, but in the case of Town Quay electrolytic action was, if not the sole cause, a very important contributory cause. The 1899 structure, which is still in excellent condition, was made with dry, low water-cement ratio concrete; the 1902 one was made with a "rather wet" mixture.

Not only is the first maritime reinforced concrete structure built in Great Britain still in excellent condition, but most concrete structures in sea-water exposures are in good condition when good practice was used and care was taken in their design and construction. For example, the concrete ship "Atlantus," the first constructed by the U. S. Government, was launched in 1918. It was brought to Cape May, New Jersey, to serve as a terminal for a ferry line and in 1927 became stranded on a sandbar. It was inspected at various times between 1918 and 1930. A report on its trial run in 1919 from Brunswick, Georgia, to Charleston, South Carolina, states that the concrete was "in a practically perfect state of preservation with no important rust stains visible, although there could be traced in certain places on the hull the faint markings of hairline cracks which paralleled the system of reinforcing closest to the outer surface." L. W. Walter in 1929¹⁸ published a photograph of a specimen of concrete taken from the ship in 1928 showing the imprint of a square bar 13/16 in., and a round bar 5/16 in. from the outer exposed surface of the concrete, and stated that the steel was not corroded. After an examination of the ship in 1928, it was reported that a very pronounced rust stain had developed in the bulkhead enclosing the afterquarters, and in one spot the bars parallel to the deck were clearly outlined for a space of 2 or 3 ft each way. A close inspection of this area showed that the coverage of concrete was almost nil. In some places the intended depth of coverage was 1/4 in.; in some cases the actual coverage was less than 1/16 in. A disk of concrete 3 in. in diameter and 0.7 in. thick was cut from a fragment collected in 1928, tested in the laboratory, and found to have very low water permeability.¹³

Similar inspection reports have been recorded on other concrete ships

built during World War I. The "Selma," now stranded near Galveston, Texas, was inspected and reported on by Mr. Ralph Rogers at the 1953 Regional Meeting of the American Concrete Institute. The "Selma" was a tanker, built in Mobile in 1918, and sunk at Galveston in about 1923. Samples of the concrete tested in 1953 showed a compressive strength of about 10,000 psi. No corrosion of steel was observed even though less than an inch of cover was provided. Another of these vessels, the "Palo Alto," is exposed on the Pacific coast at Seacliff Beach State Park, 6 miles south of Santa Cruz, California, where it is used as a fishing pier. It was built as a tanker during World War I, and is 435 ft long. It remained anchored in the Oakland Estuary, where it was built, until 1930 when the Cal-Nevada Stock Company purchased it and had it towed to Seacliff on Monterey Bay, about 100 miles to the south. The sea cocks were opened and it now rests on a sandstone shelf. It was later acquired by the State of California when the state park was created. The ship has broken its back, but a gangway across the fracture permits both parts to be used. It is probably the most accessible of the remaining World War I concrete ships.²⁰

Concluding Statement

The conclusions of the 18th Congress of the Permanent International Association of Navigation Congresses* as summarized by Warren¹⁹ are quoted as a closing statement:

* Much useful data on performance of structures exposed to sea water are contained in the publications of the Permanent International Association of Navigation Congresses (General Secretary, 155 rue de la Loi, Brussels, Belgium); e.g., "Recent evidence and new preventive measures in regard to disintegration of mortar and concrete in sea water," M. Rocha, A. Coutinho, and A. Beja Neves, Proceedings, XVII Congress, Lisbon, 1949 (Section II, Communication 2, 30 pp).

"It was agreed that the deterioration of concrete in warm sea water is mainly due to chemical action, namely, the change in composition of the cement caused by the chlorides and sulphates present in the water. Little can be done to protect poor concrete, the remedy being to select a suitable type of cement and good sound aggregates in the first place, and to take steps to ensure that the finished product is as dense and impermeable as possible. In colder water, chemical action is less severe and the main damage is done by temperature changes. There are other causes of deterioration, such as abrasion and acids deposited by lithofagous organisms."

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